

[DOCUMENT NAME] Specification

[TITLE OF THE INVENTION]

Method for Cleaning Wafers

[SCOPE OF CLAIM FOR PATENT]

[Claim 1] A method for cleaning a wafer having a step of clearing a wafer containing an inter-layered insulating layer having a surface to be subjected to a chemical mechanical polishing by using polishing slurry containing oxidizing agent after formation of a copper layer, characterized in that said step includes a first stage where removal of particles is carried out in alkaline or hydrogen reduction atmosphere produced by using one of aqueous ammonia containing ammonia at 0.0001 - 0.5 weight percent, catholyte produced around a cathode through electrolysis of pure water or water solution containing ammonia equal to or less than 0.5 weight percent and liquid produced by dissolving hydrogen in the pure water or the wafer solution containing ammonia equal to or less than 0.5 weight percent and a second stage where clearing is carried out in acidic ambience produced by using water solution containing polycarboxylic acid capable of producing chelate compound together with copper, ammonium salt and polyaminocarboxylic acid at 0.01 - 7 weight percent in the order described hereinbefore.

[Claim 2] The method for cleaning a wafer as set forth in claim 1, in which said polycarboxylic acid used in said second stage is one of oxalic acid, citric acid, malic acid, malein acid, succinic acid, tartalic acid and malonic acid, and said ammonium salt is salt of these acids.

[Claim 3] The method for cleaning a wafer as set forth in claim 1 or 2, in which said polycarboxylic acid is oxalic acid.

[Claim 4] A method for cleaning a wafer having a step of clearing a wafer containing an inter-layered insulating layer having a surface to be subjected to a chemical mechanical polishing by using polishing slurry containing oxidizing agent after formation of a tungsten layer, characterized in that said step includes a first stage where removal of particles is carried out in alkaline or hydrogen reduction atmosphere produced by using one of aqueous ammonia containing ammonia at 0.0001 - 5 weight percent, catholyte produced around a cathode through electrolysis of pure water or water solution containing ammonia equal to or less than 5 weight percent and liquid produced by dissolving hydrogen in the pure water or the wafer solution containing ammonia equal to or less than 5 weight percent and a second stage where clearing is carried out in acidic ambience produced by using water solution containing at least one of oxalic acid, ammonium oxalate and polyaminocarboxylic acid at 0.01 to 7 weight percent in the order described hereinbefore.

[Claim 5] The method for cleaning a wafer as set forth in one of claims 1 to 4, in which said the washer used in said first stage is the electrolyte or the hydrogen- containing liquid, and the oxidation-reduction potential ranges from -1000 milli-volts to - 300 milli-volts by using a silver chloride pole as a reference electrode.

[Claim 6] The method for cleaning a wafer as set forth in any one of claims 1 to 5, in which said inter-layered insulating layer used for said wafer is formed from a silicon oxide layer.

[Claim 7] The method for cleaning a wafer as set forth in any one of claims 1 to 5, in which said inter-layered insulating layer used for said wafer is formed from a low-dielectric constant layer, and said electrolyte or said hydrogen-containing liquid is produced on the basis of pure water.

[Claim 8] The method for cleaning a wafer as set forth in any one of claims 1 to 7, in which another surface is cleaned by using hydrofluoric acid and hydrogen peroxide in addition to the cleaning in the acidic ambience on said surface where the wiring structure is formed.

[DETAILED DESCRIPTION OF THE INVENTION]

[0001]

[TECHNICAL FIELD OF THE INVENTION]

The present invention relates to a method for a cleaning using wafer solution in a surface cleaning system and, more particularly, to a method for a cleaning using water solution in a surface cleaning system used in a fabrication sequence for a semiconductor device.

[0002]

[PRIOR ART]

In order to accelerate the function in logic devices, a low resistive anti-EM Cu wiring layer is indispensable. The Cu wiring layers have a groove wiring structure through a chemical mechanical polishing, i.e., CMP, because a dry etching on the Cu wiring layers is difficult. This technique is hereinlater referred to as "Cu-CMP". After the dealing, it is necessary to eliminate remaining polishing particles and Cu contaminant (together with other metallic contaminant such as Fe, Ca and K) from the surface without degradation of copper wiring layers due to unnecessary etching. This is because of the fact that the Cu particles left on the surface undesirably influence the circuit behavior through internal diffusion in the presence of the electric field stress and thermal stress. (Figure 1) Moreover, it is important to prevent the manufacturing system from cross-contamination, and it will become a key technology for manufacturing a device where DRM is mixed with logic circuits.

[0003]

There is not found any cleaning technique after Cu-CMP, and, for this reason, a post W-CMP cleaning, in which a tungsten layer is the object, will be described as an example of the post metal CMP in comparison with the Cu-CMP. In the W (Cu)-

CMP, solution, in which alumina particles or silica particles are mixed in mixture of hydrogen peroxide and oxidizing agent, is popular as polishing slurry, and the alumina particles or the silica particles left on the surface of the wafer after the CMP are equal to or greater than 30000 / wafer, and Cu contamination is equal to or greater than 10^{12} atoms/ cm².

[0004]

Cu is usually growth through a plating or CVD, and a Cu layer is possibly adhered to the lower surface of the wafer. For this reason, not only the metal contamination but also the Cu layer on the lower surface are to be eliminated after the Cu-CMP.

[0005]

Conventionally, although DHF (diluted hydrofluoric acid) is used in the metal elimination through a CMP on an oxide layer, it is known that Ti is selectively etched at high speed in the use of DHF as shown in table 1. In a wafer to be targeted in the development of the present invention, Ti is used as a barrier layer, and is further used in the form of Ti or TiN in a W plug and W wiring layer, and is used in a Cu wiring layer together with Ta. For this reason, it is difficult to use DHF as cleaner after the W-CMP in a method according to the present invention. In the post W-CMP cleaning, brushing is carried out in aqueous ammonia (0.1 - 2 weight percent) in order to remove the particles in the first stage, and a spin cleaning is carried out in citric acid in order to eliminate the contamination in the second stage as reported by I. J. Malik et al, MRS. Symp. Proc. Vol. 386, p109 (1995).

[0006]

[PROBLEMS TO BE SOLVED BY THE INVENTION]

However, the following problems are inherent in the prior art technology described hereinbefore.

[0007]

Although remaining particles are to be removed through the brushing in the aqueous ammonia (0.1 to 2 weight percent), the Cu portion of the wiring exposed to the surface are etched, and a lot of pits takes place in the Cu layer. This is because of the fact that the Cu is dissolved by producing ammonia complex through reaction between the aqueous ammonia and Cu; especially, the Cu layer is polycrystal, and, accordingly, the etching speed at the grain boundaries is large; this results in the pits.

[0008]

Thus, A cleaning technology, in which the Cu contaminant and the Cu layer on the lower surface are removed without etching the Cu- wiring layer exposed to the surface of the substrate after the CMP, is to be required.

[0009]

[0009] In the method, in which citric acid is used in the cleaning after the W-CMP, W and a barrier layer (of Ti or TiN) are not etched as shown in table 1. However, it is necessary to use it at a fairly high concentration in order to eliminate the metal contaminant such as Fe (see figure 10). This results in a large amount of cleaning cost due to the chemicals, and the chemical concentration becomes high in the waste liquid. Especially, increase of TOC (the amount of total carbon) in the waste liquid is problem due to the organic chemicals.

[0010]

[MEANS TO SOLVE THE PROBLEMS]

The present inventors contemplated the problems, and found that the Cu portion of the wiring exposed to the surface were prevented from the etching and the pits in the Cu layer by using catholyte obtained from pure water or restricting the concentration of diluted aqueous ammonia through research and development effort have been made in the first stage of cleaning with brushing and that the residual particles were effectively eliminated therefrom. Moreover, there were found that Cu contaminant was effectively removed without etching the Cu portion of the wiring layer by using oxalic acid in the cleaning and that the residual metallic concentration due to K, Ca, Fe and so forth was reduced, and the present invention was completed.

[0011]

[0011] The first invention is a method for cleaning a wafer having a step of clearing a wafer containing an inter-layered insulating layer having a surface to be subjected to a chemical mechanical polishing by using polishing slurry containing oxidizing agent after formation of a copper layer, and characterized in that the step includes a first stage where removal of particles is carried out in alkaline or hydrogen reduction atmosphere produced by using one of aqueous ammonia containing ammonia at 0.0001 - 0.5 weight percent, catholyte produced around a cathode through electrolysis of pure water or water solution containing ammonia equal to or less than 0.5 weight percent and liquid produced by dissolving hydrogen in the pure water or the wafer solution containing ammonia equal to or less than 0.5 weight percent and a second stage where clearing is carried out in acidic ambience produced by using water solution containing polycarboxylic acid capable of producing chelate compound together with copper, ammonium salt and polyaminocarboxylic acid at 0.01 - 7 weight percent in the order described hereinbefore.

[0012]

The second invention is a method for cleaning a wafer having a step of clearing a wafer containing an inter-layered insulating layer having a surface to be subjected to a chemical mechanical polishing by using polishing slurry containing oxidizing agent after formation of a tungsten layer, and

characterized in that the step includes a first stage where removal of particles is carried out in alkaline or hydrogen reduction atmosphere produced by using one of aqueous ammonia containing ammonia at 0.0001 - 5 weight percent, catholyte produced around a cathode through electrolysis of pure water or water solution containing ammonia equal to or less than 5 weight percent and liquid produced by dissolving hydrogen in the pure water or the wafer solution containing ammonia equal to or less than 5 weight percent and a second stage where clearing is carried out in acidic ambience produced by using water solution containing at least one of oxalic acid, ammonium oxalate and polyaminocarboxylic acid at 0.01 to 7 weight percent in the order described hereinbefore.

[0013]

In any one of the inventions, it is desirable that the oxidizing agent is water solution containing hydrogen peroxide, iron nitrate or both of them.

[0014]

In any one of the inventions, when the washer at the first stage is the electrolyte or the hydrogen-containing water, the oxidation- reduction potential preferably ranges from -1000 millivolts to - 300 milli- volts by using a silver chloride pole as a reference electrode and, more preferably, ranges -800 milli- volts to -600 milli- volts.

[0015]

In any one of the inventions, the inter- layered insulating layer on the wafer may be formed from a low- dielectric constant layer as well as a silicon oxide layer. In this instance, it is desirable to use the electrolyte produced from the pure water or the hydrogen- containing liquid as the washer.

[0016]

The third invention is based on the cleaning method according to the two inventions, and is a method for cleaning a wafer characterized by cleaning another surface by using hydrofluoric acid and hydrogen peroxide in addition to the cleaning in the acidic ambience on the surface where the wiring structure is formed.

[0017]

In this instance, it is preferable that the concentration of the hydrofluoric acid ranges between 0.5 to 5 weight percent and, more preferably, between 1 to 2 weight percent. Moreover, the concentration of the hydrogen peroxide ranges from 0.5 to 5 weight percent and, more preferably, from 1 to 2 weight percent.

[0018]

In the first to third inventions, it is preferable that the time period consumed in the first stage ranges from 20 seconds to 60 seconds. On the other hand, it is preferable that the time period consumed in the second stage ranges from 15 seconds to 60 seconds.

[0019]

In short, a cleaning technology according to the present invention permits a low-resistive anti-EM Cu wiring layer, a W plug and a W wiring layer to be exposed to the surface of a wafer, and is carried out after a CMP, wherein diluted catholyte or diluted aqueous ammonia and oxalic acid are successively used so as to prevent the wiring portions and, especially, the Cu portions of the wiring layers from the etching and non-wiring portions from contamination due to Cu and so forth, whereby logic devices are surely accelerated.

[0020]

[EMBODIMENTS]

First, a wafer, which is the object of a cleaning, i.e., contamination due to particles is eliminated from the wafer formed with Cu layers grown through a plating or a CVD after a CMP (chemical mechanical polishing), is shown in figure 1.

[0021]

The wafer is formed with an inter-layered insulating layer 3 on a substrate 4, barrier layers 2 covering the surfaces of grooves formed therein and Cu wiring layers 1 held in contact with the outer surfaces of the barrier layers.

[0022]

The inter-layered insulating layer 3 is formed from a Si oxide layer conventionally used, and materials, which are low in dielectric constant for reducing the static capacitance C coupled to the inter-layered insulating layer 3 in order to accelerate the device, are available. They are lower in dielectric constant ($k =$ from 1.8, $k = 3.5$ at the maximum) than Si oxide ($K = 3.9$ to 4.2). Examples are organic compound such as benzocyclobutene (BCB), parylene-N and CYTOP, inorganic compound such as xerogel and HSQ (Hydrogen Silsesquioxane) and organic/inorganic composite material such as HMO (Hydrogen peroxide (H_2O_2)/ Methylsilane-based CVD oxide. Especially, HSQ ($k = 2.8$ to 3.2) is stable, and, accordingly, is appropriate.

[0023]

Ta and TiN are preferable for the barrier layer 2, and are deposited by using PVD or CVD. After the formation of the layer 2, Cu is buried. In this stage, CVD, PVD or a plating is available. After Cu is buried, excessive Cu layer and barrier layer 2 are chemically mechanically polished, i.e., CMP is carried out by using polishing slurry containing grinding particles 7a and oxidizing agent until the inter-layered insulating layer 3 is exposed. Then, the Cu layers are isolated from one another by the inter-layered insulating layer, and the Cu wiring layers 1 are completed.

[0024]

In Cu-CMP, solution, which contains alumina particles in solution containing the

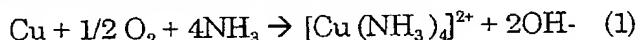
oxidizing agent such as, for example, hydrogen peroxide or iron nitride, usually serves as the polishing slurry, and the alumina particles 7a and 7b (at least 300000 / wafer) are left on the surface of the wafer after the CMP. Moreover, Cu contaminant 6a are found in the surface of the wafer at 10^{12} atoms/ cm^2 or more (in case where K and Fe are contained in the polishing slurry, Fe/ K contamination also takes place). While Cu is growing on the lower surface of the wafer, Cu is adhered so that Cu contaminant 6b at 10^{14} atoms/ cm^2 or more or a Cu layer 5 is found. It is required to eliminate the particle contaminant and the metal contaminant therefrom through a cleaning without damage to the Cu wiring layers. Residual alumina particles adhered to the wafer due to the polishing slurry are removable through a brushing. However, a chemical process is required for elimination of the metal contaminant such as Cu and other kinds of metal. In the elimination, it is necessary not to damage the Cu portions of the wiring layers. Thus, different stages are required for them.

[0025]

First, description is made on the first stage of cleaning for eliminating residual alumina particles. As described hereinbefore, the alumina particles are removal only through the mechanical brushing. However, it is important for the cleaning technology how to prevent it from re-adhesion of the particles. In order to suppress the re-adhesion, it is necessary to make the surface potential on the wafer (or brush) and the surface potential on the particles identical in sign so as to cause them electrically to repel each other. In case where alkaline solution is used as the washer, the negative polarity is given to both of the surface potential on the wafer and the surface potential on the particles so that they repel each other, thereby suppressing the re-adhesion.

[0026]

Although only aqueous ammonia is the alkaline solution which does not contaminate a semiconductor body, Cu easily produces a complex through reaction with a high concentration aqueous ammonia so as to be dissolved a shown in the following formula, and a limit is set on the concentration (pH value) of the aqueous ammonia available for the cleaning.



In case where aqueous ammonia is used as it is, it is possible to suppress the etching on the Cu portions of the wiring layers by falling the concentration in the range between 0.0001 - 0.5 weight percent so as to reduce the amount of complex produced through the reaction with Cu. Even so, it exhibits good cleaning power, and the object of the present invention is to be accomplished.

[0027]

Nevertheless, in case where better cleaning effect is expected, it is necessary to control the surface potential in the washer through another method except for the pH control, because the pH control is required for suppressing the dissolution of Cu through the production of the complex. One of the methods is usage of catholyte which is neutral but is available for controlling the surface potential.

[0028]

The catholyte is produced by using a two- vessel electrolysis system, which is introduced in "Electrochemistry Handbook", 4th edition, page 277, 1985. A system improved on the basis thereof is used for an electrolytic process for pure water.

[0029]

Raw water for the catholyte, i.e., pure water or water containing a small amount of ammonium ion (equal to or less than 0.5 weight percent) is supplied to the electrolysis vessels, and direct current voltage is applied thereinto for the electrolyte. The catholyte is obtained on the cathode side, although pH is neutral to weak base, it has a strong reducing capability due to the active hydrogen produced around the cathode, and is capable of making the surface potential on the wafer and the surface potential on the particles negative as similar to the high- concentration aqueous ammonia so as to suppress the re-adhesion.

[0030]

It was discovered that hydrogen was produced in the catholyte and, accordingly, dissolved therein. The present inventors produced a water solution through bubbling hydrogen in pure water or water solution containing a small amount of ammonia ion (equal to or less than 0.5 weight percent) which are same as the raw water of the catholyte, and confirmed that it exhibited the same cleaning capability as the above-described washer such as the catholyte.

[0031]

By the way, when any one of them is used, it is preferable to fall the oxidation-reduction potential into the rage between -1000 mV to -300 mV and, more preferably, in the range between -800 mV to -600 mV when a silver chloride pole was used as a reference electrode. The ammonia concentration in the catholyte or the hydrogen-containing water preferably ranges from 0.0005 percent to 0.01 percent, and the residual hydrogen preferably ranges from 0.1 ppm to 10 ppm. Even though the treatment is carried out, the Cu portions of the wiring layers exposed to the surface are not etched, and any pit does not take place in the Cu layers (see figure 5); and the residual particles are effectively removed (equal to or less than 100/ wafer, see figure 6).

[0032]

By the way, in the stage where the particles are to be removed, diluted aqueous ammonia, which is employed from the viewpoint of suppressing the dissolution of Cu, is controlled in such a manner that it does not produce the complex together with Cu, and, accordingly, does not have capability sufficient to removing the Cu contaminant (which is mainly oxide) from the surface after the CMP. For this reason, the Cu contaminant is selectively removed in a different way, i.e., in the second stage.

[0033]

In case where the low-dielectric constant layer, which is not the conventional Si oxide layer, is used, there is a fear of reduction in etching characteristics in the presence of the aqueous ammonia, and, for this reason, it is preferable to use the catholyte produced from pure water or the hydrogen-containing water as the washer. (table 1)

[0034]

[Table 1]

Table 1 Etching Rate on IISQ Layer and Variation of Dielectric Constant

Table 1

Washer	Etching rate (angstroms/ min)		Dielectric Constant of HSQ	
	HSQ	SiO	Before	After
NH ₄ OH (pH:9)	40	2	2.9	4.2
Catholyte from Pure water	<1	<1	2.9	2.9
Quasi-catholyte	<1	<1	2.9	2.9
Oxalic acid at 1 %	<1	<1	2.9	2.9

The second stage of the cleaning includes a cleaning step using polycarboxylic acid capable of producing copper chelate compound (at 0.05 - 7 weight percent, such as, for example oxalic acid for eliminating metal contaminant from the surface on which a wiring structure is formed and an FPM (mixture of hydrofluoric acid and hydrogen peroxide) cleaning step carried out when residual copper is left on the surface opposite to the surface on which the wiring structure is formed. As to the cleaning method,

although a spin cleaning is preferable, a mechanical cleaning using a brush is available.

[0035]

The Cu portions of the wiring layers are not etched in the oxalic acid cleaning, and the Cu contaminant is well removed (see figure 7). This is because of the fact that it has the capability to produce the chelate compound through the reaction with the Cu contaminant (CuOx) produced in the Cu-CMP. However, the Cu layer is formed through the metallic- bond, and is less etched. Since TiN, Ta, TaN and TaSiN, which form the barrier layer, do not produce any complex with the oxalic acid, they are not etched. Thus, it is possible to selectively eliminate the residual Cu contaminant from the surface without etching (or degrade) the Cu wiring layers and the barrier layers. In case where the low dielectric constant insulating layer is used as the inter- layered insulating layer, it is understood from table 1 that they are not etched in the cleaning as similar to the conventional silicon oxide layer. Experiments shown in figure 8 teaches that it is effective against not only Cu but also K, Ca, Fe and so fourth so as to reduce the residual metal contaminant to 2×10^{10} atoms/ cm² or less. In case where any Cu layer is not left on the lower surface, the water solution of oxalic acid is applicable to both surfaces. Moreover, the chemical in the solution may be at least one of other kinds of polycarboxylic acid capable of producing the chelate as similar to the oxalic acid, the ammonium salts thereof (containing oxalate) and polyaminocarboxylic acids. Examples of the polycarboxylic acid usable instead of oxalic acid are citric acid, D-tartaric acid, L-tartaric acid, malein acid, malonic acid, malic acid and ammonium salts thereof. Although the activation capability is not so large as the other examples, succinic acid can produce a chelate compound. Good cleaning capability is achieved by prolonging the time.

[0036]

As described hereinbefore, it is possible to eliminate the particle contaminant and the metallic contaminant such as the Cu contaminant from the wafer surface without any damage to the Cu wiring layers by virtue of the present method.

[0037]

There remains a case where Cu layer is left on the lower surface during the growth of Cu. Not only the metallic contaminant but also the Cu layer are to be eliminated therefrom. In this case, the upper surface is treated with the oxalic acid for cleaning and the Cu contaminant and the excess Cu layer is removed from the lower surface by using FPM (mixture of hydrofluoric acid and hydrogen peroxide, HF : H₂O₂ : H₂O = 1-10 : 1-10 : 200). FPM is capable of oxidizing and dissolving the Cu layer produced in

the metallic bond so as to effectively remove it. However, DHF (water solution of hydrofluoric acid) is not effective, because Cu is not ionized.

[0038]

By using FPM (mixture of hydrofluoric acid and hydrogen peroxide) as the washer, the it is possible to reduce the Cu concentration to 2×10^{10} atoms/ cm^2 or less and other metallic contaminant (such as K and Fe) to also 2×10^{10} atoms/ cm^2 or less (as will be understood from figure 10 showing the experimental results). Thus, it is possible to effectively eliminate the polishing particles and the metallic contaminant such as, for example Cu without damaging the Cu layers and the barrier metal (such as TiN, Ta, TaN and TaSiN) from the upper surface of the wafer and the excess Cu from the lower surface by virtue of the present cleaning method.

[0039]

Subsequently, a wafer, from which the polishing particles are eliminated after the CMP on a surface formed with W layers through CVD or a sputtering as described in conjunction with the prior art, is shown in figure 2.

[0040]

The wafer includes an inter-layered insulating layer 3 covering the surface of a Si substrate 4, wiring layers 12 (of Al or Cu) formed in grooves previously formed in the inter-layered insulating layer 3, barrier layers 11 (of TiN or Ti) and W plugs 10 held in contact with the exposed surfaces of the barrier layers.

[0041]

It is preferable to form the inter-layered insulating layer 3 of a low dielectric constant material such as, for example, HSQ as well as Si oxide.

In W-CMP, solution, which is mixture of oxidizing agent containing hydrogen peroxide and Fe nitrate in addition with silica particles, is used as polishing slurry, and silica particles 9a and 9b remain on the surfaces of the wafer (at equal to or greater than 30000 / wafer) after the CMP. Moreover, Fe contaminant 8a (and K/ Cu contaminant 8b if certain polishing slurry is used) is left on the surfaces of the wafer at 10^{12} atoms/ cm^2 or more.

[0042]

It is necessary to remove the particle contamination and the metal contamination without damage to the W plugs and the W wiring layers. Basically, the sequence is similar to that of the cleaning after the Cu-CMP.

[[0043]

In the first stage, the particles are removed through brushing in use of aqueous ammonia (0.0001 - 5 weight percent), catholyte or hydrogen- containing water

(ammonia concentration: 0- 5 weight percent). Since W is less dissolved in relatively high-concentration ammonia, it is not necessary to be careful in the cleaning after W-CMP like that for Cu.

[0044]

In the second stage, the cleaning is carried out in the water solution of oxalic acid (0.01 - 5 weight percent) in order to remove the metal contamination. The chemical contained therein may be the oxalic acid, ammonium oxalate or one of the polyaminocarboxylic acids. However, the citric acid is not available as described in connection with the prior art. A centrifugal spray cleaning is desirable for the second stage, and, alternatively, a brushing is available for the second cleaning. Moreover, the lower surface may be treated with FPM as similar to the cleaning after the Cu-CMP.

[0045]

Since polishing slurry containing Fe nitrate is popular in the W-CMP, it is necessary to effectively eliminate Fe contaminant equal to or greater than 10^{12} atoms/ cm^2 . The Fe on the Si oxide layer is in the form of FeOx, and, accordingly, is easily removable through producing the complex by virtue of the chelate effect of the oxalic acid. Even if it is relatively low in concentration, the sufficient removal effect is achieved rather than citric acid reported in use of the W-CMP. (Figure 11) However, it does not produce any complex with the W plugs and the barrier layers of Ti and TiN because of the metal bonding, and, accordingly, does not etch them. (table 2)

[0046]

[Table 2]

Table 2 Etching rate (angstrom/ min)

	Cu	TiN	Ta	TaN	W	Ti
Oxalic acid (0.1 %)	< 1	< 1	< 1	< 1	< 1	< 1
Citric acid (5 %)	< 1	< 1	< 1	< 1	< 1	< 1
DHF (0.5 %)	2	< 1	< 1	< 1	< 1	50

Thus, the polishing particles and the metal contaminant such as Fe are effectively eliminated from the surfaces of the wafer without any damage to the W plugs, the W wiring layers and the barrier metal (TiN, Ti).

[0047]

Subsequently, description proceeds to the operation. Figure 3 shows a flowchart showing the sequence of the cleaning.

[0048]

Wafers are placed in a loader of a cleaning system dipped in water after the Cu-CMP in order to prevent them from drying. This is because of the fact that the polishing particles are less eliminated from dried wafers. It is preferable to supply fresh pure water to the loader at all times. This is because of the fact that the oxidizing agent on the wafers tends to be dissolved into the wafer so as to erode the Cu wiring layers. From this viewpoint, wafers may be stored under being sprayed at all times instead of the dipping.

[0049]

Since Cu is much eroded rather than W, it is preferable to wash the wafers immediately after the CMP, and the CMP apparatus and the cleaning apparatus may be combined into an in-line type system.

[0050]

The cleaning is carried out through two stages as shown in figure 4.

[0051]

In order to eliminate the alumina particles in the first stage, both surfaces of a wafer is treated with brushing for 20 seconds to 60 seconds by using aqueous ammonia (at 0.001 weight percent, by way of example). The brushing may be of the rolling brushes shown in figure 4; otherwise, it may be disk type. As to the supply of the aqueous ammonia, it may be dropped onto the brushes or onto the wafer in the vicinity of the brushes. Otherwise, it may be supplied to the inside of the brushes.

[0052]

Catholyte may be supplied as the washer. The catholyte used therein is, by way of example, produced from pure water through electrolysis, and the pH and the oxidation-reduction potential (with reference electrode: AgCl) are 7.0 and -650 mV, respectively. Otherwise, the catholyte may be produced from aqueous ammonia containing a small amount of ammonia so that the pH and the oxidation-reduction potential are 8.2 and -770 mV, respectively. Hydrogen may be dissolved into the pure water or the aqueous ammonia through bubbling.

[0053]

After the treatment with the aqueous ammonia, the ammonia may be eliminated from both surfaces of the wafer through rinse by using pure water for 5 seconds to 20 seconds.

[0054]

In order to eliminate the metal contaminant from the upper surface, a spin cleaning is carried out by using oxalic acid (at 0.5 percent, by way of example) in the second stage, and the Cu contaminant and excess Cu layer are removed from the lower surface by using FPM (HF: H₂O₂: H₂O = 1: 1: 100, by way of example). The time period consumed therein is of the order of 15 seconds to 30 seconds, and the rinsing is carried out with pure water for 10 seconds to 30 seconds.

[0055]

The waiting time between the first stage and the second stage is minimized by equalizing the time period consumed by the treatment with the chemicals and the time period consumed by the rinsing.

[0056]

It is preferably perfectly isolate the cleaning chamber for the first stage (which is carried out in the alkaline atmosphere) and the cleaning chamber for the second stage (which is carried out in the acidic atmosphere). The reason is to suppress the production of salt.

[0057]

When the cleaning and the rinsing are completed, the wafers are subjected to a spin drying, and is conveyed to the unloader.

[0058]

The cleaning method after the Cu-CMP has been described; the basic sequence after the W-CMP is similar thereto. W is less eroded and oxidized in comparison with Cu, and it is not necessary to carry out the cleaning immediately after the CMP like Cu. However, it is preferable to clean the W without leaving it in the water for a long time.

[0059]

[Examples]

Although the present invention is hereinbelow described in detail by showing examples, the present invention is never limited to the examples. The conventional Si oxide layer was used as the inter-layered insulating layer 3 in all the wafers of examples, samples for experiments and comparative examples.

[0060]

(Example 1)

Cleaning after Cu- CMP

The wafers were dipped into water after the Cu-CMP in order to prevent them from drying in the loader of the cleaning apparatus, and the cleaning was immediately carried out by means of the in-line type system.

[0061]

The cleaning was carried out through the two stages as shown in figure 4.

[0062]

In order to eliminate the alumina particles in the first stage, both surfaces of the wafer was treated with the aqueous ammonia (at 0.001 weight percent) and brushed for 20 seconds to 60 seconds. The rolling brushes shown in figure 4 were used in the brushing.

[0063]

Upon completion of the treatment with the aqueous ammonia, the ammonia was eliminated from both surfaces of the wafer through rinsing in pure water for 5 seconds to 20 seconds.

[0064]

In the second stage, the metallic contaminant was eliminated from the upper surface through the spin cleaning by using oxalic acid (at 0.5 weight percent), and the Cu contaminant and the residual Cu layer were removed by using FPM (HF: H_2O_2 : H_2O = 1: 1: 100). The cleaning consumed 15 seconds to 30 seconds, and the rinsing was carried out in pure water for 10 seconds to 30 seconds.

[0065]

The cleaning chamber for the first stage (in the alkaline atmosphere) was perfectly isolated from the cleaning chamber for the second stage (in the acidic atmosphere) so as to prevent them from salt.

[0066]

When the cleaning and the rinsing were completed, the wafer was dried by means of a spin dryer, and was, thereafter, conveyed to the unloader.

[0067]

(Second Example)

It was carried out under the same conditions as the first example except that the catholyte, which was produced from the pure water so that the pH and the oxidation-reduction potential were 7.0 and -650 mV (by using the reference electrode: AgCl), was used in the first stage.

[0068]

(Third example)

It was carried out under the same conditions as the first example except that the concentration of oxalic acid was changed to 0.1 weight percent in the second stage.

[0069]

(Fourth example)

It was carried out under the same conditions as the first example except that citric

acid at 5 weight percent was used in the second stage.

[0070]

(Fifth example)

In order to evaluate the anti-etching capability, extremely low concentration aqueous ammonia (at 0.0002 weight percent) was used in the cleaning in the first stage, and, thereafter, the etching rate on the Cu layers and the residual particles were determined. This evaluation was also carried out by using the catholyte used in the second example.

[0071]

Moreover, experiments a little different from the examples were carried out. They were fallen within the embodiments in a broad sense, and were referred to as "samples".

[0072]

(Sample 1)

Using the catholyte used in the second embodiment and the diluted aqueous ammonia (at 0.0002 weight percent) used in the fifth embodiment, dipping was continued for 10 minutes, and pits were counted in unit length after the etching.

[0073]

(Sample 2)

The first stage was carried out under the same conditions as the first embodiment, dipping was carried out for 2 minutes in the second stage, and the following organic acid (concentration: 1 weight percent) was used for the cleaning.

[0074]

oxalic acid, citric acid, malic acid, malein acid, succinic acid, tartalic acid, malonic acid

(Comparative Sample 1)

It was carried out under the same conditions as the first example, but aqueous ammonia at 1.8 weight percent was used. The same measurement was carried out as similar to the fifth example and sample 1.

[0075]

(Comparative Sample 2)

Citric acid used in the fourth example was used for the treatment on the lower surface of the first example.

[0076]

(Result, Part 1)

Figures 5 to 10 show the results of the first example to the fifth example, the results

of samples 1 and 2 and the result of comparative sample 1. Figure 5 shows the evaluation of the second example, the fifth example, sample 1 and the comparative sample 1 from the viewpoint of anti-etching capability. As to the second and fifth examples, the etching was suppressed on the Cu wiring layers, because the ammonia concentration was restricted. However, the Cu wiring layers of comparative sample 1 were seriously etched due to the high ammonia concentration.

[0077]

Figure 6 shows the number of residual contamination particles counted on the examples and the comparative samples; there was not significant difference among them, even though the ammonia concentration was restricted, the number of residual particles was reduced.

[0078]

Figure 7 shows the evaluation on the third example and the fourth example from the viewpoint of the final elimination capability to the metallic contaminant such as K, Ca and Cu (oxide). In the third example, it (i.e., oxalic acid at 0.1 percent) effectively eliminated the metallic contaminant therefrom and prevented them, although the effect was slightly weak, the fourth example (citric acid at 5 percent) reached the practical use.

[0079]

Figure 8 shows evaluation results on the first example, second example and comparative sample 2 from the viewpoint of the metallic contamination eliminating capability. Ta was used for the barrier layers. There was not significant difference between the aqueous ammonia and the catholyte produced from pure water in the first stage, and good metallic contamination eliminating capability of oxalic acid was corroborated in comparison between the cleaning in the second stage and the cleaning without the second stage.

[0080]

Figure 9 shows the result of sample 2 in comparison with that before the cleaning, and teaches that the Cu elimination capability was good in any kind of polycarboxylic acid. Although only the succinic acid exhibited the capability lower than the others, it was to be considered to cope therewith by prolonging the cleaning time and/ or increasing the concentration.

[0081]

Figure 10 shows the evaluation on the first example and comparative sample 2 from the viewpoint of the metallic contamination (which was mainly Cu layer) eliminating capability from the lower surface. Comparing it with that before the cleaning on the

lower surface, although the citric acid (used in comparative sample 2) was effective against K and Fe, there was not any effect against the Cu metallic layer. On the other hand, the Cu layer was effectively eliminated by virtue of FPM in the first example.

[0082]

(Example 6)

Cleaning After W-CMP

Wafers were cleaned through the two stages after the W-CMP as similar to that after the Cu-CMP.

[0083]

In the first stage, aqueous ammonia (at 0.0001 weight percent) was used and brushing was carried out in order to eliminate silica particles.

[0084]

In the second stage, spin cleaning was carried out in oxalic acid (at 0.05 weight percent, 0.1 percent, 0.5 percent, 1 percent and 5 percent in weight) in order to eliminate the metallic contaminant.

[0085]

(Comparative Sample 3)

Citric acid (at 0.05 percent, 0.1 percent, 0.5 percent, 1 percent and 5 percent in weight) was used in the second stage under the same conditions as the fifth example.

[0086]

(Result, Part 2)

Figure 11 shows the evaluation of the fifth example and comparative sample 3 from the viewpoint of the Fe elimination capability from the surface. As to the fifth example, the etching in the W wiring layers was suppressed, and Fe contaminant was almost eliminated. However, even though fairly high concentration washer was used in comparative sample 3, Fe contaminant was left.

[0087]

[EFFECTS OF THE INVENTION]

According to the present invention, the first stage, in which diluted aqueous ammonia or catholyte is used, is combined with the second stage, in which oxalic acid and FPM (water solution of hydrofluoric acid and hydrogen peroxide) are used, in the surface cleaning after the Cu-CMP on the wiring layers of a high speed logic device, the contaminant due to the metals including the Cu and W outside the wiring portion is effectively eliminated and suppressed without damage to the Cu wiring layer, W plug and barrier layer.

[BRIEF DESCRIPTION OF THE DRAWINGS]

[Fig. 1] is a schematic view showing the wafer after the Cu-CMP.

[Fig. 2] is a schematic view showing the wafer after the W-CMP.

[Fig. 3] is a flowchart showing the cleaning sequence according to the present invention.

[Fig. 4] is a view showing the concept of the cleaning method according to the present invention.

[Fig. 5] is a graph showing the amount of Cu etched and the number of pits after the brushing on the Cu layer.

[Fig. 6] is a graph showing the residual particles after the cleaning carried out after the Cu-CMP.

[Fig. 7] is a graph showing the metallic contaminant concentration on the surface of the wafer after the cleaning after the Cu-CMP.

[Fig. 8] is a graph showing the metallic contamination eliminating capability in the oxalic acid cleaning (brushing) after the Cu-CMP.

[Fig. 9] is a graph showing the Cu contaminant elimination capability of various kinds of chelate producible dicarboxylic acid after the Cu-CMP.

[Fig. 10] is a graph showing the concentration of metallic contaminant on the lower surface of the wafer after the cleaning after the Cu-CMP.

[Fig. 11] is a graph showing the concentration of the metallic contaminant on the surface of the wafer after the cleaning after the W-CMP.

[BRIEF DESCRIPTION OF REFERENCES]

1... Cu wiring layer, 2... barrier layer (Ta, TiN, TaN, TaSiN), 3... inter-layered oxide layer, 4... Si substrate, 5... adhered Cu layer, 6a.. Cu contaminant (adhered to the upper surface of wafer), 7a... polishing particles (adhered to the upper surface of wafer), 6b... Cu contaminant (adhered to the lower surface of wafer), 7b... polishing particles (adhered to the lower surface of wafer), 8a... Fe contaminant (adhered to the upper surface of wafer), 8b... Cu contaminant (adhered to the lower surface of wafer), 9a... polishing particles (adhered to the upper surface of wafer), 9b ... polishing particles (adhered to the lower surface of wafer), 10... W plug, 11 ... barrier layer (Ti, TiN), 12 ... wiring layers (Al, Cu), 13 ... wafer, 14a ... brush (for upper surface of wafer), 14b .. brush (for lower surface of wafer).

[DOCUMENT NAME] ABSTRACT

[ABSTRACT]

[PROBLEM] To provide a method for effectively eliminating metallic contaminant including Cu layer from a wafer after CMP necessary for Cu wiring layers and W plugs provided in ULSI for a high- speed logic operation without damage to the wiring layers and the plugs.

[SOLVING MEANS] Keeping the surfaces moisture, a cleaning is carried out in aqueous ammonia, catholyte or hydrogen containing water with brushing without a long time interval from the CMP in the first stage in alkaline atmosphere, and, thereafter, a spin cleaning or brushing is carried out in washer containing at least one of chelate producible polycarboxylic acid such as oxalic acid, ammonium salt thereof and polyaminocarboxylic acid in the second stage in acidic atmosphere; if necessary, the lower surface is treated with washer containing hydrofluoric acid and hydrogen peroxide in the second stage for eliminating a residual Cu layer and metallic contaminant.

[SELECTED FIGURE] figure 3

[DOCUMENT NAME] DRAWINGS

[Fig. 1] 1.. Cu wiring, 2... barrier layer (Ta, TiN), 3... inter- layered insulating layer, 4 ... Si substrate,

(Upper surface) 6a... Cu contaminant, 7a ... polishing particles,

(Lower surface) 5... adhered Cu layer, 6b... Cu contaminant, 7b... polishing particles

[Fig. 2] 3... inter-layered insulating layer, 4... Si substrate, 10... W plug, 11... barrier layer (TiN, Ti), 12 ... wiring layer (Al, Cu)

(Upper surface) 8a... Fe contaminant, 9a.. polishing particle

(Lower surface) 8b... Cu contaminant, 9b... polishing particles

[Fig. 3] first block... [Cu-CMP (W-CMP)], second block... [dipped in water together with loader], third block... [first stage for eliminating particle elimination: cleaning using brush (catholyte, diluted aqueous ammonia, hydrogen containing water), fourth block... [rinse in pure water], fifth block... [second stage for eliminating metallic contamination: spin cleaning (upper surface... oxalic acid; lower surface... FPM or oxalic acid), sixth block.... [rinse in pure water], seventh block ... [drying]

[Fig. 4]

left block ... [first stage]

arrows... catholyte or

aqueous ammonia

right block... [second stage]

upper arrow... water solution of

oxalic acid

lower arrow... FPM

[Fig. 5]

Etching rate of Cu layer (angstroms/ min.)

The number of pits per unit length of Cu

Etching

The number of pits

Comparative Example 5

Sample (aqueous ammonia 0.0002%) (catholyte from aqueous ammonia 1.8 %) pure water

Example 2

solubility from
pure water)

(*) : sample 1

[Fig. 6]

Equal to or greater than 30000/ wafer before cleaning

The number of residual Particles after cleaning (/ wafer)	1	Cleaning through brushing (60 sec) on P-TEOS
	1	
	1	
	1	

Fig. 7

The amount of residual meal on surface	Before cleaning	After cleaning in Citric acid (5%) (example 4)	After cleaning in Oxalic acid (0.1%) (example 3)
1	1	1	1
2	2	2	2
3	3	3	3
4	4	4	4
5	5	5	5
6	6	6	6
7	7	7	7
8	8	8	8
9	9	9	9
10	10	10	10

Fig. 8

The amount of meal contaminant on wafer surface (atoms/cm ²)	aqueous ammonia (before treatment with oxalic acid) aqueous ammonia → oxalic acid (example 1) catholyte → oxalic acid (example 2)	P-TEOS surface after Cu/Ta-CMP

[Fig. 9]

Residual		dipping for 2 min.
Cu concentration		
on surface		
(atoms / cm ²)		

Before oxalic citric malic malein succinic tartalic malonic
cleaning acid acid acid acid acid acid acid

Concentration of these kinds of organic acid: 1 %

(Sample 2)

[Fig. 10]

Concentration		Lower surface of wafer
of metallic		
contaminant		
on wafer surface		

Before	Comparative sample	Example 1
cleaning	(citric acid: 5%)	(FPM)

[Fig. 11]

Upper surface of wafer (W-CMP)

Concentration of		
Fe contaminant		Comparative sample 4 (citric acid)
on wafer surface		
		example 6 (oxalic acid)

Concentration of washer (%)

Regards